

REMARKS/ARGUMENTS

The claims remain as 1 to 10.

Examiner Harlan is thanked for the interview courteously granted Applicants' representative on April 22, 2004. The following includes the presentation made at that interview.

Claim 1 is amended to delineate the invention with greater clarity. No new issues are raised.

"Conducting the polymerization" replaces polymerizing.

The necessarily implied step of "initiating the polymerization of the monomers" is positively recited. This is done by heating the polymerization vessel contents, and/or by allowing the polymerization to proceed, as disclosed in the paragraph at page 10, line 13.

The addition of the anti-foam agent (A) and the partially saponified polyvinyl alcohol (B) is stating to be continuous, in a positive manner, as recited in original Claim 1 and disclosed in the paragraph at page 7, line 17 of the specification.

The final clause "from said polymerization vessel" is removed as superfluous.

Re: Claim Rejections - 35 U.S.C. § 102

Reconsideration and withdrawal of the rejection of Claims 1-2 and 4-10 under 35 U.S.C. § 102(b) as being anticipated by Wierer et al., U.S. Patent No. 5,314,530 (hereinafter "Wierer") are requested.

The Official Action states that:

Wierer teaches a process for preparing under emulsion or suspension polymerization conditions, vinyl chloride using an anti-foam agent, polyvinyl alcohol, and in some cases an olefinic comonomer.

The Official Action recognizes the reasons for Applicants' position that Wierer et al. do not anticipate because, it is stated therein:

8. The Applicants argue Wierer teaches a foam stabilizer, not an anti-foam agent.

The Official Action however indicates that:

The Examiner contends that the two terms are in fact synonymous and have the same purpose.

At the noted interview Applicants presented prior art citations that indicate that the two terms are not synonymous and relate to different functions performed by different reagents.

The text Surfactants and Interfacial Phenomena, 1978, by M.J. Rosen (pages 218-220 attached) states at page 218, in the first sentence in the second paragraph under "Section IV, Foam-Stabilizing Organic additives", that:

Additives that increase the rate of attainment of surface tension equilibrium act as foam inhibitors by decreasing film elasticity while those that decrease the rate of attainment of that equilibrium act as foam stabilizers.

The text on page 218 under Section IV, page 218 treat foam-stabilizing additives and under Section V, page 220 anti-foaming agents.

Kirk-Othmer, Encyclopedia of Chemical Technology, 4th Ed. vol. 7, at pages 928-930 treats defoamers and their functions. Silicone oil is discussed on page 930, 2nd paragraph.

Vol. 11, at pages 797 and 798, of Kirk-Othmer, treat foams for fire-fighting and their advantages. The use of foaming agents is briefly discussed at page 798, 2nd paragraph.

Copies of the above are enclosed.

Clearly, Wierer et al. want to keep their foam stable so that it can be applied to a textile substrate to produce a flame retardant coating having a foam structure.

Since Applicants want to destroy the foam generated during polymerization of monomers, they employ an anti-foam agent. The benefit is that the foams formed during polymerization, which contain much polymer, are broken and thereby polymer deposition in the reflux condenses and on the upper parts of the polymerization vessel is significantly diminished. All of this is discussed in the application and summarized in the paragraph at page 8, line 8.

Clearly, then Wierer et al. do not anticipate Applicants for the above reasons.

In addition, Wierer et al. do not disclose the continuous addition of an anti-foaming additive which Applicants emphasize. The additive is to be added during polymerization while the reflux condenser is operating and during recovery of monomer. The reasons for such continuous addition is set forth at page 7, line 17 of the specification.

Nor does Wierer et al. disclose starting the continuous addition during operation of the reflux condenser.

In fact, Wierer et al. do not disclose adding a foam stabilizer to a polymerizing mixture of monomers. Hence, they do not disclose controlling the foam produced during polymerization.

With regard to the Examiner's first question, page 4 of the Official Action, in the present invention, the components (A) and (B) are added to defoam the polymerization mixture in the polymerization vessel; namely, foam should be preferably reduced or suppressed quickly. However, to the contrary, the foam stabilizer used in Wierer et al. ('530) means to keep foam long or to improve the lifetime of foam, as clear from the description in column 2, lines 53-60; column 5, lines 33-35 and column 6, lines 3-40 (particularly, lines 3-12). The coating composition of '530 must be applied and dried in the form of a foam, because this form appreciably improves the vapor permeability. For this reason, the foam must be mechanically produced beforehand, and the foam must not

disappear quickly but its life must be prolonged until the completion of the coating operation.

Thus, the anti-foam agent of (A) is entirely different from the foam stabilizer of '530.

Applicants therefore urge that Wierer et al. do not anticipate the rejected claims.

Re: Claim Rejection - 35 U.S.C. § 103

Reconsideration and withdrawal of the rejection of Claim 3 under 35 U.S.C. § 103(a) as being unpatentable over Wierer et al. in view of Coleman, U.S. Patent No. 4,230,843 (hereinafter "Coleman") are also requested.

The Official Action justifies the rejection as follows:

The present claim 3 differs from Wierer in that Wierer does not teach the use of a silicone anti-foam agent. Silicon anti-foaming agents PVC preparations are common as exemplified in the examples section. See Coleman, col. 17, line 6. In view of Coleman, one having an ordinary skill in the art would be motivated to modify Wierer by using a silicone anti-foam agent.

However, in Applicants' view, as discussed above, Wierer et al. are interested in foam stabilization. As discussed in the above-noted literature citations, an anti-foaming agent has an effect which is the antithesis of foam stabilization. Hence, Wierer et al. would not be motivated to employ a silicone anti-foaming agent based upon the Coleman disclosure.

Coleman et al. is also silent as to the combined use of (A) and (B). If an anti-foam agent is used singly, foaming cannot be controlled effectively as shown by Comparative Examples 4 and 5.

It is therefore Applicants' view that the rejection is not sustainable.

Re: Claim Rejections - 35 U.S.C. § 112

Reconsideration and withdrawal of the rejection of Claim 1 under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicant regards as the invention are requested.

The Official Action states several reasons for the rejection, as follows:

First the process claims reads as two separate processes.

Actually, the Claim 1 stated “starting to add (A)... and (B).... to the polymerization system during polymerization and during the operation of said reflux condenser”. Hence, it would appear that there was sufficient tie-in of the identified “two separate processes”.

The present claim language recites “to the polymerization mixture in said polymerization vessel during the operation of the reflux condenser”. It is believed that identified “two separate processes” are clearly tied-in as one. The polymerization mixture in said “polymerization vessel” clearly contains vinyl chloride.

The Official Action then states:

Furthermore, “the polymerization system” and “the recovery of unreacted monomers” lack an antecedent basis. Also, what does “starting to add” mean?

The first quote is replaced by “the polymerization mixture in said polymerization vessel” and is thus sufficiently determinative. “The recovery of unreacted monomers” refers back to “polymerization of the monomers” in the amended claim and is sufficiently determinative in its reference to “unreacted monomers”.

As for “starting to add”, it did not stand alone. It was part of the clause “starting to add ... during polymerization”. However, the present language “starting the continuous additions” appears appropriate to distinguish from simply “adding”.

The expression “mainly vinyl chloride” was discussed at the interview. It was considered defined at page 4, the paragraph at line 18.

Entry of the amendment as raising no new issues and favorable reconsideration are solicited.

Respectfully submitted,

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Surfactants and Interfacial Phenomena

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surfactants decreases to a very small volume in a few minutes (Kuwamura, 1972). Placing methyl groups at the ends of the polyoxyethylene chains away from the hydrophobic group, in these cases, too, produces even lower foam volumes and foam stabilities, together with larger surface areas per molecule (Takahashi, 1973).

IV. FOAM-STABILIZING ORGANIC ADDITIVES

The foaming properties of surfactant solutions can be modified greatly by the presence or addition of other organic materials. Solutions that show excellent foaming properties can be converted to low- or nonfoaming materials and those that show poor foaming properties can be converted to high-foaming products by the addition of small amounts of the proper additive. Because of its practical importance, this method of modifying foaming properties has been extensively used and investigated.

Additives that increase the rate of attainment of surface tension equilibrium act as foam inhibitors by decreasing film elasticity while those that decrease the rate of attainment of that equilibrium act as foam stabilizers. Additives that decrease the rate of attainment of surface tension equilibrium may do so by decreasing the critical micelle concentration of the surfactant solution, thereby lowering the activity of the monomeric surfactant in solution and its rate of migration to the surface. On the other hand, additives that cause the breakdown of micelles, with the consequent increase in the activity of the monomeric surfactant, increase the rate of attainment of surface tension equilibrium and decrease foaming (Ross, 1958). Another mechanism by means of which additives can act as foam stabilizers is by increasing the mechanical strength of foam films. The surface films produced by solutions of highly purified surfactants are often weakly coherent films, containing molecules that are relatively widely spaced because of the mutual repulsion of the oriented polar heads. These films are mechanically weak and nonviscous. When they constitute the interfacial film in the lamellae of a foam, liquid drains rapidly from the lamellae. The addition of the proper additive to this type of film can convert it to a closer-packed, more coherent one of high surface viscosity, which is slow-draining and produces a much more stable foam.

The most effective additives for increasing the stability of the foam produced by surfactant solutions appear to be long-chain, often water-insoluble, polar compounds with straight-chain hydrocarbon groups of approximately the same length as the hydrophobic group

of the surfactant. Examples are lauryl alcohol for use with sodium dodecyl sulfate, *N,N*-bis(hydroxyethyl) lauramide for use with dodecylbenzenesulfonate, lauric acid for use with potassium laurate, and *N,N*-dimethyldodecylamine oxide for use with dodecylbenzenesulfonate and other anionics.

Studies of the effectiveness of these additives in stabilizing the foam of various types of anionic surfactants indicate that the foam produced by straight-chain surfactants is more susceptible to stabilization than that produced by branched-chain materials. The order of "susceptibility" to foam stabilization is as follows: primary alkyl sulfates > 2-*n*-alkanesulfonates > secondary alkyl sulfates > *n*-alkylbenzenesulfonates > branched-chain alkylbenzenesulfonates (Sawyer, 1958). This is exactly the order of decreasing van der Waals interaction with an adjacent compound containing a straight-chain hydrocarbon group. Moreover, the most effective foam stabilizing compounds are those that lower the CMC of the surfactant solution considerably (Schick, 1957). Since the CMC of a surfactant in aqueous solution is not lowered significantly by solubilization of the material into the interior of the micelle, but only by solubilization between the surfactant molecules in the outer portion of the micellar case, the so-called palisade layer (Chapter 3, Section IV, C), it appears that the additive operates by penetrating into the surface film and organizing the surfactant molecules into a condensed structure by orienting itself between the molecules of surface-active agent in the film in a manner similar to that in the palisade layer of a micelle.

The increased cohesion of the resulting film may be due to the presence of a nonionic, polar "buffer" between the mutually repelling ionic heads of the surfactant molecules to which both ionic heads are attracted by ion-dipole interactions, whereas the hydrocarbon portions of all the molecules are held together by van der Waals forces. This would account for the greater susceptibility of surfactants having straight-chain hydrophobic groups to foam boosting and for the greater effectiveness of additives having straight-chain hydrophobic groups.

Polar additives may also increase foam stabilization by solubilizing foaming oils (Schick, 1957), since micelles containing solubilized polar additives (Chapter 4, Section I, B, 4) have increased solubilization power for nonpolar materials.

The nature of the polar group in these additives is important. It has been found (Sawyer, 1958) that the order of effectiveness in these additives is *N*-polar substituted amides > unsubstituted amides > sulfolanyl ethers > glycerol ethers > primary alcohols. This order

may be that of decreasing ability to form H-bonds with the adjacent surfactant and water molecules since film viscosity increases greatly where H-bonding between adjacent molecules is possible. The OH group in an alcohol is *not* capable sterically of forming direct bonds with adjacent molecules containing only OH groups, whereas the $-\text{CONH}-$ group is capable of direct bonding with adjacent molecules. Also, foam stabilization is greater for those additives containing more than one polar group capable of forming hydrogen bonds. The explanation given for this is that the multiple hydrogen bonds with water prevent the polar additives from being forced out from between the surfactant molecules and into the interior of the micelles in the bulk phase.

Another foam stabilizer for anionic surfactants, *N,N*-dimethyldodecylamine oxide, appears to operate in a somewhat different manner. Here it has been shown (Kolp, 1963; Rosen, 1964) that interaction occurs between the protonated amine oxide cation, $\text{RN}(\text{CH}_3)_2\text{OH}^+$ and the surfactant anion, yielding a product that has been isolated, $\text{RN}(\text{CH}_3)_2\text{OH}^+ \cdot \text{O}_3\text{SR}^-$, in which cation and anion are very strongly H-bonded via the H^+ of the cation. This compound is much more surface active than either the amine oxide or the anionic surfactant and adsorbs strongly at the air/water interface to form a very closely packed film (Rosen, 1964). Similarly, salts of long-chain amines and alkyl sulfonates of equal chain length, for example, $\text{C}_{10}\text{H}_{21}\text{SO}_3^- \cdot ^+\text{N}(\text{CH}_3)_3\text{C}_{10}\text{H}_{21}$, have been shown to produce unusually stable thin aqueous films because strong electrical attraction between the cationic and anionic surface-active ions promotes formation of a close-packed surface film (Corkill, 1963).

V ANTIFOAMING

Antifoaming agents appear to operate by replacing the foam-producing surface film by an entirely different type of film. To do this, they must displace any foam stabilizer, such as surfactants, present in the film. They must, therefore, have a surface tension low enough in the pure state so that they can spread spontaneously over the existing film. This means that their spreading coefficients, $S_{L/S} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA}$ (equation 6.1), must be positive. They must also maintain a high concentration in the surface while being used at very low concentrations. Therefore they must be quite insoluble in the foaming solution, but still not so insoluble in it that they do not become a component of the surface film.

References

Two types are used: foam breakers and foam inhibitors. Foam breakers are materials that destroy existing foam. They may act (1) by reducing the surface tension in local areas to exceptionally low values, thereby causing these local areas to be thinned rapidly to the breaking point by the pull of the surrounding higher tension regions [ethyl ether ($\gamma = 17$ dynes/cm) acts in this manner, as does also *i*-amyl alcohol in small amount (Okazaki, 1960)] and (2) by promoting drainage of the liquid from the foam film and thereby shortening its life. Tributyl phosphate acts in this manner by reducing surface viscosity sharply. Its large cross-sectional area in the interfacial film may cause it to reduce cohesive forces between surfactant molecules when it fits between them in the interfacial film.

Foam inhibitors are materials that prevent foam from being formed. They act by eliminating surface elasticity. They produce a surface that has a substantially constant surface tension when subjected to expansion or contraction. Some inhibitors do this by swamping the surface with nonfoaming, rapidly diffusing, noncohesive, only moderately surface-active molecules, so that any transient rise in surface tension caused by film expansion is rapidly annulled. Some wetting agents and ethylene oxide-propylene oxide block copolymers appear to act in this manner. Others act by replacing the elastic surface film with a brittle, close-packed surface film. Calcium salts of long-chain fatty acids (stearic and plamitic) do this with the foam of sodium dodecylbenzenesulfonate or sodium lauryl sulfate by displacing it from the surface film and replacing it wholly or in part by calcium soap molecules that form a "solid," brittle film having no elasticity. This calcium soap film consequently produces an unstable foam. If the calcium soap can form a true mixed film with the surfactant, the foam is *not* destroyed by the calcium soap (Peper, 1958).

At least in some cases, the foam-breaking and foam-inhibiting properties appear to be additive, and mixtures of a foam breaker and a foam inhibitor show remarkably good foam-breaking and foam-inhibiting properties (Okazaki, 1960).

REFERENCES

- Broich F., *Seifen-Ole-Fette-Wachse* 92, 853 (1966).
 Brown, A. G., W. C. Thuman and J. W. McBain, *J. Colloid Sci.* 8, 491 (1953a).
 Brown, A. G., W. C. Thuman and J. W. McBain, *J. Colloid Sci.* 8, 508 (1953b).

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DEFOAMERS

The control or elimination of the foam that occurs in many industrial processes is often a key factor in their efficient operation. The additives that are used in low concentration to achieve this effect are known variously as defoamers, antifoaming agents, foam inhibitors, and foam controllers. Defoaming implies breaking a pre-existing foam whereas antifoaming or foam inhibition indicates prevention of the formation of that foam. Such distinctions call for different product features. A defoamer is expected to exhibit rapid knockdown of a foam, whereas longevity of action might be the key requirement in many antifoam applications. Despite these varying performance features, many applications require both preventive and control functions, and in practice the same types of materials are used both for antifoaming and defoaming. For this reason, the general term defoamers, as used in this article, is meant to encompass all product types and degrees of action encountered with such process aids. The topic is sometimes known as chemical (physicochemical would be better) foam control as opposed to thermal and mechanical foam control, such as centrifuging or spraying of the foam or the use of ultrasound, which are not covered here.

Many industries now rely on the efficient and economical use of defoamers both as a process aid in product manufacture and to increase the quality of the finished product in its subsequent application. The most obvious use of defoamers as process aids is to increase holding capacity of vessels and improve efficiency of distillation or evaporation equipment. They are also used to improve filtration, dewatering, washing, and drainage of suspensions, mixtures, or slurries. Examples of industrial operations that benefit in these ways from the use of defoamers include oil well pumping; gas scrubbing at petrochemical plants; polymer and chemical synthesis and processing, particularly in monomer stripping; textile dyeing and finishing; leather processing; paint and adhesive manufacture; phosphoric acid production; control of wastewater and sewage; food preparation, notably the refining of sugar; the brewing of beer; and penicillin production by fermentation. Among the finished products that are improved in quality or efficacy by the proper inclusion of defoamers are lubricants, particularly cooling lubricants in metal working; diesel fuel, hydraulic and heat-transfer fluids; paints and other coatings; adhesives; inks; detergents; and antifatulence tablets.

The use of vegetable and mineral oils as defoamers has been known for a long time. However, most modern defoamers are complex, formulated specialty chemicals. They are usually proprietary products and the patent literature is the best guide to their probable composition. Patent surveys (1,2) are particularly valuable sources of information. Other useful reviews include those in encyclopedias and handbooks (3-5), some of which have a special focus on defoamers in coatings (4) and on polymer aspects of defoaming (5). Companies involved in the production of defoamers range from large, basic polymer producers to small regional formulators. In addition to control of foam and associated features such as rate of foam knockdown and the persistence of the effects, other frequently needed application requirements of these specialty materials include adequate shelf life, absence of adverse effects on and by the products being treated, ease of handling, lack of toxicity to manufacturing personnel and users, environmental acceptabil-

ity, and cost-effective oils to costly fluctuations that matters, but Another factor to ancillary surface

Classification of

Modern defoamer product requirements schemes is possible chemical type. Classification of general defoamers in liquid states and agents, thickening water. Not all defoamulations contain

ACTIVE INGREDIENTS

These are the components that control work. They are homogeneous solutions of hydrophobic solid particles in a carrier. They are classified as carriers.

Liquid-Phase

nature of the polymer, phosphate, etc. Because since this effect is present, it is preferred to approach identifies the silicones, and fluorine

Many similar naphthenic mineral oil, soybean oil (80% as defoamers. Liquid poly(alkylene oxide) are also used. Organic defoamers and have a class of hydrocarbons, 2,4,7,9-tetramethyls, agricultural products

Numerous other (5); these include polyamines, polyalcohols, molecular weight resins

ity, and cost-effectiveness. Defoamers range from relatively inexpensive mineral oils to costly fluorinated polymers but it is not the cost per kilogram of defoamer that matters, but rather the cost per unit produced using this processing aid. Another factor that strongly influences the choice of a specific defoamer is its ancillary surface properties such as wetting, dispersion, and leveling.

Classification of Defoamers

Modern defoamers typically contain numerous ingredients to meet the diverse product requirements for which they are formulated. A variety of classification schemes is possible including classification by application, physical form, and chemical type. Classification by chemical type is a very satisfactory approach. In general defoamers contain a variety of active ingredients in both the solid and liquid states and numerous ancillary agents such as emulsifiers, spreading agents, thickeners, preservatives, carrier oils, compatibilizers, solvents, and water. Not all defoamers contain all classes of components; some complex formulations contain several compounds in some of the categories.

ACTIVE INGREDIENTS

These are the components of the formulation that do all or most of the actual foam control work. Traditionally, defoamers were single component liquids or homogeneous solutions of vegetable or mineral oils, but more recently a number of active hydrophobic solids have been utilized so effectively that in a dispersion of hydrophobic solids in a traditional oil such as castor oil [8001-79-4], the oil could be classed as a carrier oil rather than an active ingredient.

Liquid-Phase Components. It is usual to classify organic liquids by the nature of the polar or hydrophilic functional group, ie, alcohol, acid, ester, phosphate, etc. Because lowering of surface tension is a key defoamer property and since this effect is a function of the nonpolar portion of the liquid-phase component, it is preferable to classify by the hydrophobic, nonpolar portion. This approach identifies four liquid phase component classes: hydrocarbons, polyethers, silicones, and fluorocarbons.

Many similar hydrocarbon fluids such as kerosene and other paraffinic and naphthenic mineral oils and vegetable oils such as linseed oil [8001-26-1], corn oil, soybean oil [8001-22-7], peanut oil, tall oil [8000-26-4], and castor oil are used as defoamers. Liquid fatty alcohols, acids and esters from other sources and poly(alkylene oxide) derivatives of oils such as ethoxylated rosin oil [68140-17-0] are also used. Organic phosphates (6), such as tributyl phosphate, are valuable defoamers and have particular utility in latex paint applications. Another important class of hydrocarbon-based defoamer is the acetylenic glycols (7), such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol which are widely used in water-based coatings, agricultural chemicals, and other areas where excellent wetting is needed.

Numerous organic polymers have also been proposed as foam control agents (5); these include polyisobutylene [9003-27-4], poly(alkyl acrylates), polyalkylene polyamines, polyalkyleneimines, and a variety of other copolymers and low molecular weight resins. Poly(alkylene oxide) homopolymers and copolymers are fre-

quently encountered in liquid-phase antifoam components. For example, copolymers [106392-12-5] of poly(ethylene oxide) and poly(propylene oxide) are used to reduce foam in the acid-gas scrubbing process (8). High molecular weight adducts of propylene oxide and polyhydric alcohols such as glycerol [56-81-5] and pentaerythritol [115-77-5] have also been reported to have useful antifoaming properties (3). Sometimes the polyether is mixed with other liquids, eg poly(propylene oxide) [25322-69-4] and polydimethylsiloxane [9016-00-6]; sometimes the two materials are copolymerized.

Silicone oils are particularly effective antifoaming agents in nonaqueous systems because of their low surface tension and incompatibility. Polydimethylsiloxane (PDMS) is the most important silicone and is widely used in products for the petroleum industry, where its good thermal stability is very advantageous (9). Other useful silicone defoamers are polytrifluoropropylmethylsiloxanes [25791-89-3] and other fluorosilicones, which are very effective in nonaqueous foaming systems such as organic solvents and crude hydrocarbon stocks. Fluorocarbons are the most expensive class of antifoam fluid. Fluorocarbon oils and fluorine-containing amides such as the *N*-(alkylamino-trimethylene)perfluorooctanamides are used as antifoaming additives to lubricants and jet fuels (10).

Solid-Phase Components. Dispersed solids are vital ingredients in commercial antifoam formulations. Much of the current theory on antifoaming mechanism ascribes the active defoaming action to this dispersed solid phase with the liquid phase primarily a carrier fluid, active only in the sense that it must be surface-active in order to carry the solid particles into the foam films and cause destabilization. For example, polydimethylsiloxane, despite its considerable effectiveness in nonaqueous systems, shows little foam-inhibiting activity in aqueous surfactant solutions. It is only when compounded with hydrophobic silica [7631-86-9] to give the so-called silicone antifoam compounds that highly effective aqueous defoamers result. Using the same classification adopted for liquids, gives three solid phase component classes: hydrocarbons, silicones, and fluorocarbons.

A variety of waxy hydrophobic hydrocarbon-based solid phases are used including fatty acid amides and sulfonamides, hydrocarbon waxes such as montan wax [8002-53-7], and solid fatty acids and esters. The amides are particularly important commercially. One example is the use of ethylenediamine distearamide [110-30-5] as a component of latex paint and paper pulp black liquor defoamer (11). Hydrocarbon-based polymers are also used as the solid components of antifoaming compositions (5); examples include polyethylene [9002-88-4], poly(vinyl chloride) [9002-86-2], and polymeric ion-exchange resins.

In most cases, these active defoaming components are insoluble in the defoamer formulation as well as in the foaming media, but there are cases which function by the inverted cloud-point mechanism (3). These products are soluble at low temperature and precipitate when the temperature is raised. When precipitated, these defoamer-surfactants function as defoamers; when dissolved, they may act as foam stabilizers. Examples of this type are the block polymers of poly(ethylene oxide) and poly(propylene oxide) and other low HLB (hydrophilic-lipophilic balance) nonionic surfactants.

Pure silicone solids, such as silicone resins, are used in defoamer formulations, but the key material in this category is hydrophobic silica, listed here because the hydrophobic treatment is usually a silicone polymer or silane monomer.

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such as shaving creams, the aerosol technique is especially suitable (39) (see AEROSOLS). Hydrocarbons or chlorofluorocarbons are liquefied at high pressure and then emulsified with the surfactant solution. When released to atmospheric pressure, the propellant droplets evaporate into tiny gas bubbles which aggregate into a foam.

Applications

Foams have a wide variety of applications that exploit their different physical properties. The low density, or high volume fraction of gas, enable foams to float on top of other fluids and to fill large volumes with relatively little fluid material. These features are of particular importance in their use for fire fighting. The very high internal surface area of foams makes them useful in many separation processes. The unique rheology of foams also results in a wide variety of uses, as a foam can behave as a solid, while still being able to flow once its yield stress is exceeded.

Foams are also widely encountered in circumstances where their presence is detrimental. Foams are common to many processes that entail agitation of fluids or bubbling of air through fluids. The presence of any type of surface-active ingredient, even in minute quantities, enhances the formation of foams in the processing. The presence of the foams increases the volume of the fluids and makes them more difficult to process and transport. Moreover, foams can have strong detrimental environmental effects. Thus, just as the production and stabilization of foams is important in some industrial processes, so the elimination of foams is crucial in many others. As a result, a wide variety of defoaming agents have been developed to eliminate or reduce the formation of foams (see DEFOAMERS).

Firefighting. Foams are widely used in firefighting applications (40). They are particularly useful in extinguishing flammable liquids, eg, gasoline. Whereas water simply agitates the gasoline, further spreading the fire, and then sinks to the bottom of the burning fluid, a foam is less dense than the burning liquid, and remains suspended on its surface. The collapsing bubbles cool the fluid near the surface, and reduce the amount of oxygen available to the flame, ultimately extinguishing it. A foam is also a more efficient use of the firefighting liquid, typically water, enabling it to be spread over a much larger area.

Foams for firefighting applications are typically made from a concentrated foaming agent diluted with water and then mixed with air. Rather than consider the volume fraction of air in the foam, firefighting foams are characterized by their expansion ratio, which is the increase in volume of the liquid after the foam is formed. Expansion ratios range from 5:1 to over 1000:1; ratios of 5:1 to 20:1 are called low expansion; ratios of 21:1 to 200:1, medium expansion; and ratios greater than 200:1, high expansion.

Low expansion foams are used most commonly. Because they are relatively more dense, they can more easily be sprayed larger distances, making them safer to use. In addition, because of the larger amount of liquid, they are more resistant to the heat of the fires, making them more effective as extinguishers. Their primary disadvantage is the relatively smaller area that they can cover due to their

lower expansion ratio. Medium expansion foams are usually too light to be sprayed any distance, and instead must be formed very near to the flames. However, they can cover a much larger area of flame, and the low density reduces the probability of disrupting the surface of the burning fluid. They are less heat resistant and hence more easily destroyed than low expansion foams. However, they can cover a much greater area. High expansion foams cover the widest area, but suffer from even poorer heat resistance, and virtually no ability to be sprayed. Hence they are typically formed in place, and are often used to fill the places where a fire has already started, such as in the holds of ships, warehouses, or mines. They are also sometimes used in fighting forest fires in areas where water is scarce.

Most foam-forming concentrates used contain some form of protein, usually derived from animals. In addition, many contain fluorochemical surfactants to increase their foaming performance. Other foaming agents are comprised solely of synthetic surfactants. Most foams produced with either protein-based or synthetic foaming agents are susceptible to polar fluids, particularly alcohols, which are miscible in water and tend to destroy the firefighting foams. As a result, all-purpose foaming agents have been developed that produce foams which are not destroyed by alcohols, and are effective in fighting all types of fires. They typically contain natural polymers that are insoluble in polar solvents.

Food. Foams are common to a wide variety of food products. Whipped cream and meringue are essentially foams, and ice cream is comprised of a large amount of foam. These foams are stabilized by proteins; the two most important are egg white and milk proteins. For food products, it is desirable not only to achieve good foaming properties, but also to form stable foams (41-44). The ease with which foams are formed depends on the capacity of the proteins to rapidly adsorb onto the interface. The stability of the foams depends on the ability of the proteins to form an elastic membrane at the interface, which both prevents bubble coalescence and is sufficiently impermeable to reduce gas diffusion. One of the best food-foaming agents is egg white or egg albumen. It consists of a mixture of different proteins, each serving a particular function (45). Globulins are the most surface-active agents, leading to good foamability; drainage is retarded by the high viscosity caused by globulins and ovomucoids; the film strength is enhanced by surface complexes formed between lysozymes and ovomucins. Upon heating, thermal denaturation of ovalbumin and conalbumin results in a more permanent foam structure, leading to its widespread use in baked products. Ice cream is also a type of foam possessing varying amounts of air bubbles incorporated during an aeration step in the processing (46). These bubbles are initially stabilized by milk proteins, primarily β -casein, α -lactalbumin, and β -lactoglobulin (47). Further stabilization occurs due to the adsorption of fat globules on the interface.

Another important digestible foam is that on the top of a glass of freshly poured beer (qv). Although not as long lasting, it is nevertheless considered an important aesthetic quality of the beverage, and is thus the subject of considerable research (48,49). In addition, its aesthetic importance is somewhat dependent on location. For example, beer in the United Kingdom has traditionally possessed a higher and longer lasting head of foam than that in the United States. The foam in beer is usually formed by the dissolved CO_2 , although dissolved nitrogen has also been used to improve the quality. The main stabilizer in the foam is proteins

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